

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

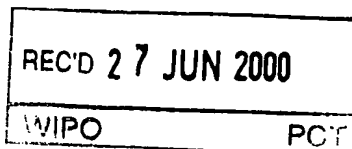
**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

THIS PAGE BLANK (USPTO)

09/762363

Eur päisches
PatentamtEur pean
Patent OfficeOffice eur péen
des brevets

EP 00 / 3333



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99201172.6

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE,
LA HAYE, LE

31/05/00

THIS PAGE BLANK (USPTO)



Eur päisches
Patentamt

European
Patent Office

Office eur péen
des brevets

Blatt 2 d r B sch inigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°: 99201172.6

Anmeldetag:
Date of filing: 15/04/99
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
Monsieur Technology Company bv
2132 MS Hoofddorp
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Components and catalysts for the polymerization of olefins

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

/

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

THIS PAGE BLANK (USPTO)

TC 5405

TITLE:

“COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS”

The present invention relates to catalyst components for the polymerization of olefins, to the catalysts obtained therefrom and to the use of said catalysts in the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms. In particular the present invention relates to catalyst components, suitable for the stereospecific polymerization of olefins, comprising Ti, Mg, halogen and an electron donor compound selected from esters of substituted succinic acids (substituted succinates). Said catalyst components when used in the polymerization of olefins, and in particular of propylene, are capable to give polymers in high yields and with high isotactic index expressed in terms of high xylene insolubility.

The chemical class of succinates is known in the art. However, the specific succinates of the present invention have never been used as internal electron donors in catalysts for the polymerization of olefins.

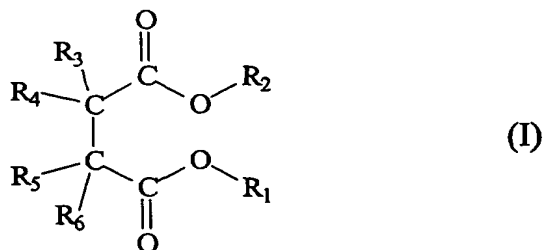
EP-A-86473 mentions the use of unsubstituted succinates as internal donors in catalyst components for the polymerization of olefins. The use of diisobutyl succinate and di-n-butyl succinate is also exemplified. The results obtained in terms of isotactic index and yields are however poor.

The use of polycarboxylic acid esters, including succinates, as internal donors in catalyst components for the polymerization of olefins, is also generically disclosed in EP 125911. Diethyl methylsuccinate and diallyl ethylsuccinate are mentioned in the description although they are not exemplified. Furthermore, EP263718 mentions, but does not exemplify the use of diethyl methylsuccinate and di-n-butyl ethylsuccinate as internal donors. In order to check the performances of these succinates according to the teaching of the art the applicant has carried out some polymerization tests employing catalyst components containing diethyl methylsuccinate and diisobutyl ethylsuccinate respectively as internal donors. As shown in the experimental section, both the so obtained catalysts gave an unsatisfactory activity/stereospecificity balance very similar to that obtained with catalysts containing unsubstituted succinates.

It has been therefore very surprising to discover that the specific substitution in the succinates of the invention generates compounds that, when used as internal donors, give catalyst components having excellent activity and stereospecificity.

(TC 5405.EP)

It is therefore an object of the present invention to provide a solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbon radical with 1-12 carbon atoms, comprising Mg, Ti, halogen and an electron donor selected from succinates of formula (I):



wherein the radicals R_1 and R_2 , equal to or different from each other, are a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; the radicals R_3 to R_6 equal to or different from each other, are hydrogen or a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms, further, the radicals R_3 to R_6 which are joined to the same carbon atom can be linked together to form a cycle; with the proviso that when R_3 to R_5 are contemporaneously hydrogen R_6 is a radical selected from primary branched, secondary or tertiary alkyl groups, cycloalkyl, aryl, arylalkyl or alkylaryl groups having from 3 to 20 carbon atoms.

R_1 and R_2 are preferably $\text{C}_1\text{-C}_8$ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. Particularly preferred are the compounds in which R_1 and R_2 are selected from primary alkyls and in particular branched primary alkyls. Examples of suitable R_1 and R_2 groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, neopentyl, 2-ethylhexyl. Particularly preferred are ethyl, isobutyl, and neopentyl.

One of the preferred groups of compounds described by the formula (I) is that in which R_3 to R_5 are hydrogen and R_6 is a branched alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl radical having from 3 to 10 carbon atoms. Particularly preferred are the compounds in which R_6 is a branched alkyl group or a cycloalkyl group having from 3 to 10 carbon atoms.

Specific examples of suitable monosubstituted succinate compounds are diethyl

phenylsuccinate, diethyl cyclohexylsuccinate, diethyl benzylsuccinate, diethyl cyclohexylmethylsuccinate, diethyl t-butylsuccinate, diethyl isobutylsuccinate, diethyl isopropylsuccinate, diethyl neopentylsuccinate, diethyl isopentylsuccinate, diethyl (1,1,1-trifluoro-2-propyl)succinate, diethyl (9-fluorenyl)succinate, diethyl tetradecylsuccinate, diisobutyl phenylsuccinate, diisobutyl cyclohexylsuccinate, diisobutyl benzylsuccinate, diisobutyl cyclohexylmethylsuccinate, diisobutyl t-butylsuccinate, diisobutyl isobutylsuccinate, diisobutyl isopropylsuccinate, diisobutyl neopentylsuccinate, diisobutyl isopentylsuccinate, diisobutyl (1,1,1-trifluoro-2-propyl)succinate, diisobutyl tetradecylsuccinate, diisobutyl (9-fluorenyl)succinate, dineopentyl phenylsuccinate, dineopentyl cyclohexylsuccinate, dineopentyl benzylsuccinate, dineopentyl cyclohexylmethylsuccinate, dineopentyl t-butylsuccinate, dineopentyl isobutylsuccinate, dineopentyl isopropylsuccinate, dineopentyl neopentylsuccinate, dineopentyl isopentylsuccinate, dineopentyl (1,1,1-trifluoro-2-propyl)succinate, dineopentyl tetradecylsuccinate, dineopentyl (9-fluorenyl)succinate.

Another preferred group of compounds within those of formula (I) is that in which at least two radicals from R_3 to R_6 are different from hydrogen and are selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms. Particularly preferred are the compounds in which the two radicals different from hydrogen are linked to the same carbon atom, that is R_3 and R_4 or R_5 and R_6 . Specific examples of suitable disubstituted succinates are: diethyl 2,2-dimethylsuccinate, diethyl 2-ethyl-2-methylsuccinate, diethyl 2-Benzyl-2-isopropylsuccinate, Diethyl 2-cyclohexylmethyl-2-isobutylsuccinate, Diethyl 2-cyclopentyl-2-n-butylsuccinate, Diethyl 2,2-diisobutylsuccinate, Diethyl 2-cyclohexyl-2-ethylsuccinate, Diethyl 2-isopropyl-2-methylsuccinate, Diethyl 2-tetradecyl-2-ethylsuccinate, Diethyl 2-isobutyl-2-ethylsuccinate, Diethyl 2-(1,1,1-trifluoro-2-propyl)-2-methylsuccinate, Diethyl 2-isopentyl-2-isobutylsuccinate, Diethyl 2-phenyl-2-n-butylsuccinate, diisobutyl 2,2-dimethylsuccinate, diisobutyl 2-ethyl-2-methylsuccinate, Diisobutyl 2-benzyl-2-isopropylsuccinate, Diisobutyl 2-cyclohexylmethyl-2-isobutylsuccinate, Diisobutyl 2-cyclopentyl-2-n-butylsuccinate, Diisobutyl 2,2-diisobutylsuccinate, Diisobutyl 2-cyclohexyl-2-ethylsuccinate, Diisobutyl 2-isopropyl-2-methylsuccinate, Diisobutyl 2-tetradecyl-2-ethylsuccinate, Diisobutyl 2-

isobutyl-2-ethylsuccinate, Diisobutyl 2-(1,1,1-trifluoro-2-propyl)-2-methylsuccinate, Diisobutyl 2-isopentyl-2-isobutylsuccinate, Diisobutyl 2-phenyl-2-n-butylsuccinate, dineopentyl 2,2-dimethylsuccinate, dineopentyl 2-ethyl-2-methylsuccinate, Dineopentyl 2-Benzyl-2-isopropylsuccinate, Dineopentyl 2-cyclohexylmethyl-2-isobutylsuccinate, Dineopentyl 2-cyclopentyl-2-n-butylsuccinate, Dineopentyl 2,2-diisobutylsuccinate, Dineopentyl 2-cyclohexyl-2-ethylsuccinate, Dineopentyl 2-isopropyl-2-methylsuccinate, Dineopentyl 2-tetradecyl-2-ethylsuccinate, Dineopentyl 2-isobutyl-2-ethylsuccinate, Dineopentyl 2-(1,1,1-trifluoro-2-propyl)-2-methylsuccinate, Dineopentyl 2-isopentyl-2-isobutylsuccinate, Dineopentyl 2-phenyl-2-n-butylsuccinate.

Furthermore, also the compounds in which the two radicals different from hydrogen are linked to different carbon atoms, that is R_3 and R_5 or R_4 and R_6 are particularly preferred. Specific examples of suitable compounds are diethyl 2,3-dibenzylsuccinate, diethyl 2,3-diisopropylsuccinate, diethyl 2,3-bis(cyclohexylmethyl)succinate, Diethyl 2,3-di-t-butylsuccinate, Diethyl 2,3-diisobutylsuccinate, Diethyl 2,3-dineopentylsuccinate, Diethyl 2,3-diisopentylsuccinate, Diethyl 2,3-diphenylsuccinate, Diethyl 2,3-dicyclohexylsuccinate, diethyl 2,3-dicyclopentylsuccinate, Diethyl 2,3-bis(1,1,1-trifluoro-2-propyl)succinate, Diethyl 2,3-bis(tetradecyl)succinate, Diethyl 2,3-bis(9-fluorenyl)succinate, Diethyl 2-isopropyl-3-isobutylsuccinate, Diethyl 2-t-butyl-3-isopropylsuccinate, Diethyl 2-isopropyl-3-cyclohexylsuccinate, Diethyl 2-isopentyl-3-cyclohexylsuccinate, Diethyl 2-tetradecyl-3-cyclohexylmethylsuccinate, Diethyl 2-cyclohexyl-3-cyclopentylsuccinate, diisobutyl 2,3-dibenzylsuccinate, diisobutyl 2,3-diisopropylsuccinate, diisobutyl 2,3-bis(cyclohexylmethyl)succinate, Diisobutyl 2,3-di-t-butylsuccinate, Diisobutyl 2,3-diisobutylsuccinate, Diisobutyl 2,3-dineopentylsuccinate, Diisobutyl 2,3-diisopentylsuccinate, Diisobutyl 2,3-diphenylsuccinate, Diisobutyl 2,3-dicyclohexylsuccinate, Diisobutyl 2,3-dicyclopentylsuccinate, Diisobutyl 2,3-bis(1,1,1-trifluoro-2-propyl)succinate, Diisobutyl 2,3-bis(tetradecyl)succinate, Diisobutyl 2,3-bis(9-fluorenyl)succinate, Diisobutyl 2-isopropyl-3-isobutylsuccinate, Diisobutyl 2-t-butyl-3-isopropylsuccinate, Diisobutyl 2-isopropyl-3-cyclohexylsuccinate, Diisobutyl 2-isopentyl-3-cyclohexylsuccinate, Diisobutyl 2-tetradecyl-3-cyclohexylmethylsuccinate, Diisobutyl 2-cyclohexyl-3-cyclopentylsuccinate, dineopentyl 2,3-dibenzylsuccinate, dineopentyl 2,3-

(TC 5405.EP)

diisopropylsuccinate, dineopentyl 2,3-bis(cyclohexylmethyl)succinate, Dineopentyl 2,3-di-*t*-butylsuccinate, Dineopentyl 2,3-diisobutylsuccinate, Dineopentyl 2,3-dineopentylsuccinate, Dineopentyl 2,3-diisopentylsuccinate, Dineopentyl 2,3-diphenylsuccinate, Dineopentyl 2,3-dicyclohexylsuccinate, Dineopentyl 2,3-dicyclopentylsuccinate, Dineopentyl 2,3-bis(1,1,1-trifluoro-2-propyl)succinate, Dineopentyl 2,3-bis(tetradecyl)succinate, Dineopentyl 2,3-bis(9-fluorenyl)succinate, Dineopentyl 2-isopropyl-3-isobutylsuccinate, Dineopentyl 2-*t*-butyl-3-isopropylsuccinate, Dineopentyl 2-isopropyl-3-cyclohexylsuccinate, Dineopentyl 2-isopentyl-3-cyclohexylsuccinate, Dineopentyl 2-tetradecyl-3-cyclohexylmethylsuccinate, Dineopentyl 2-cyclohexyl-3-cyclopentylsuccinate.

Furthermore, particularly preferred are the compounds in which at least three radicals from R_3 to R_6 are different from hydrogen and are selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms. Specific examples of suitable compounds are diethyl 2-isobutyl-2,3-dimethylsuccinate, diethyl 2,3-diisobutyl-3-isopropylsuccinate, diethyl 2,3-diphenyl-3-methylsuccinate, diethyl 2-methyl-2-isobutyl-3-phenylsuccinate, diethyl 2-cyclohexyl-2-*n*-propyl-3-ethylsuccinate, diethyl 2,2,3-trimethylsuccinate, diethyl 2-benzyl-3-ethyl-3-methylsuccinate, diethyl 2-cyclohexylmethyl-3-ethyl-3-methylsuccinate, diethyl 2,2,3,3-tetramethylsuccinate, diethyl 2,3-diisobutyl-2,3-dimethylsuccinate, diethyl 2,3-diisobutyl-2,3-diisopropylsuccinate, diethyl 2,3-diphenyl-2,3-dimethylsuccinate, diethyl 2-methyl-2-isobutyl-3-phenyl-3-ethylsuccinate, diethyl 2-cyclohexyl-2-*n*-propyl-3,3-diethylsuccinate, diisobutyl 2-isobutyl-2,3-dimethylsuccinate, diisobutyl 2,3-diisobutyl-3-isopropylsuccinate, diisobutyl 2,3-diphenyl-3-methylsuccinate, diisobutyl 2-methyl-2-isobutyl-3-phenylsuccinate, diisobutyl 2-cyclohexyl-2-*n*-propyl-3-ethylsuccinate, diisobutyl 2,2,3-trimethylsuccinate, diisobutyl 2-benzyl-3-ethyl-3-methylsuccinate, diisobutyl 2-cyclohexylmethyl-3-ethyl-3-methylsuccinate, diisobutyl 2,3-diisobutyl-2,3-dimethylsuccinate, diisobutyl 2,3-diisobutyl-2,3-diisopropylsuccinate, diisobutyl 2,3-diphenyl-2,3-dimethylsuccinate, diisobutyl 2-methyl-2-isobutyl-3-phenyl-3-ethylsuccinate, diisobutyl 2-cyclohexyl-2-*n*-propyl-3,3-diisobutylsuccinate, diisobutyl 2,2,3,3-tetramethylsuccinate, dineopentyl 2-isobutyl-2,3-dimethylsuccinate, dineopentyl 2,3-diisobutyl-3-isopropylsuccinate, dineopentyl 2,3-diphenyl-3-methylsuccinate, dineopentyl 2-methyl-2-isobutyl-3-phenylsuccinate,

(TC 5405.EP)

dineopentyl 2-cyclohexyl-2-n-propyl-3-ethylsuccinate, dineopentyl 2,2,3-trimethylsuccinate, dineopentyl 2-benzyl-3-ethyl-3-methylsuccinate, dineopentyl 2-cyclohexylmethyl-3-ethyl-3-methylsuccinate, dineopentyl 2,2,3,3-tetramethylsuccinate, dineopentyl 2,3-dineopentyl-2,3-dimethylsuccinate, dineopentyl 2,3-dineopentyl-2,3-diisopropylsuccinate, dineopentyl 2,3-diphenyl-2,3-dimethylsuccinate, dineopentyl 2-methyl-2-isobutyl-3-phenyl-3-ethylsuccinate, dineopentyl 2-cyclohexyl-2-n-propyl-3,3-dineopentylsuccinate.

As mentioned above the compounds according to formula (I) in which two or four of the radicals R_3 to R_6 which are joined to the same carbon atom are linked together to form a cycle are also preferred.

Specific examples of suitable compounds are 1-(ethoxycarbonyl)-1-(Ethoxyacetyl)-2,6-dimethylcyclohexane, 1-(ethoxycarbonyl)-1-(Ethoxyacetyl)-2,5-dimethylcyclopentane, 1-(ethoxycarbonyl)-1-(Ethoxyacetylmethyl)-2-methyl-cyclohexane, 1-(ethoxycarbonyl)-1-(Ethoxyacetylcyclohexyl)cyclohexane.

As explained above, the catalyst components of the invention comprise, in addition to the above electron donors, Ti, Mg and halogen. In particular, the catalyst components comprise a titanium compound, having at least a Ti-halogen bond and the above mentioned electron donor compound supported on a Mg halide. The magnesium halide is preferably $MgCl_2$ in active form which is widely known from the patent literature as a support for Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

The preferred titanium compounds used in the catalyst component of the present invention are $TiCl_4$ and $TiCl_3$; furthermore, also Ti-haloalcoholates of formula $Ti(OR)_nX_y$, where n is the valence of titanium and y is a number between 1 and n, can be used.

The preparation of the solid catalyst component can be carried out according to several methods.

(TC 5405.EP)

According to one of these methods, the magnesium dichloride in an anhydrous state and the succinate of formula (I) are milled together under conditions in which activation of the magnesium dichloride occurs. The so obtained product can be treated one or more times with an excess of TiCl_4 at a temperature between -80 and $+135^\circ\text{C}$. This treatment is followed by washings with hydrocarbon solvents until chloride ions disappeared. According to a further method, the product obtained by co-milling the magnesium chloride in an anhydrous state, the titanium compound and the substituted succinate is treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane etc. The treatment is carried out for a time between 1 and 4 hours and at a temperature ranging from 40°C to the boiling point of the halogenated hydrocarbon. The product obtained is then generally washed with inert hydrocarbon solvents such as hexane.

According to another method, magnesium dichloride is preactivated according to well known methods and then treated with an excess of TiCl_4 at a temperature of about -80 to 135°C which contains, in solution, a succinate of formula (I). The treatment with TiCl_4 is repeated and the solid is washed with hexane in order to eliminate any non-reacted TiCl_4 .

A further method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to U.S. 4,220,554) and an excess of TiCl_4 comprising the succinate of formula (I) in solution at a temperature of about 80 to 120°C .

According to a preferred method, the solid catalyst component can be prepared by reacting a titanium compound of formula $\text{Ti}(\text{OR})_n\text{X}_y$, where n is the valence of titanium and y is a number between 1 and n , preferably TiCl_4 , with a magnesium chloride deriving from an adduct of formula $\text{MgCl}_2 \cdot p\text{ROH}$, where p is a number between 0.1 and 6, preferably from 2 to 3.5, and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100 to 130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054 and USP 4,469,648. The so obtained adduct can be directly reacted with the Ti compound or it can be previously subjected to thermal controlled dealcoholation (80 to 130°C) so as to obtain an adduct

in which the number of moles of alcohol is generally lower than 3 preferably between 0.1 and 2.5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold TiCl_4 (generally 0°C); the mixture is heated up to $80\text{--}130^\circ\text{C}$ and kept at this temperature for 0.5-2 hours. The treatment with TiCl_4 can be carried out one or more times. The succinate of formula (I) can be added during the treatment with TiCl_4 . The treatment with the electron donor compound can be repeated one or more times.

The preparation of catalyst components in spherical form is described for example in European Patent Applications EP-A-395083, EP-A-553805, EP-A-553806, EPA-601525 and WO98/44001.

The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and $500\text{ m}^2/\text{g}$ and preferably between 50 and $400\text{ m}^2/\text{g}$, and a total porosity (by B.E.T. method) higher than $0.2\text{ cm}^3/\text{g}$ preferably between 0.2 and $0.6\text{ cm}^3/\text{g}$. The porosity (Hg method) due to pores with radius up to 10.000 \AA generally ranges from 0.3 to $1.5\text{ cm}^3/\text{g}$, preferably from 0.45 to $1\text{ cm}^3/\text{g}$.

A further method to prepare the solid catalyst component of the invention comprises halogenating magnesium dihydrocarbyloxy compounds, such as magnesium dialkoxide or diaryloxy, with solution of TiCl_4 in aromatic hydrocarbon (such as toluene, xylene etc.) at temperatures between 80 and 130°C . The treatment with TiCl_4 in aromatic hydrocarbon solution can be repeated one or more times, and the substituted succinate is added during one or more of these treatments.

In any of these preparation methods the desired succinate of formula (I) can be added as such or, in an alternative way, it can be obtained *in situ* by using an appropriate precursor capable to be transformed in the desired electron donor compound by means, for example, of known chemical reactions such as esterification, transesterification, etc. Generally, the succinate of formula (I) is used in molar ratio with respect to the MgCl_2 ranging from 0.01 to 1 and preferably from 0.05 to 0.5.

The solid catalyst components according to the present invention are converted into catalysts for the polymerization of olefins by reacting them with organoaluminum compounds according to known methods.

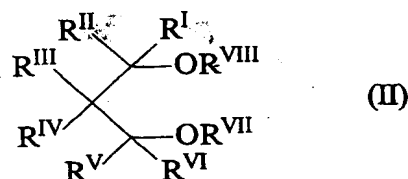
In particular, it is an object of the present invention a catalyst for the polymerization of olefins

$\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (a) a solid catalyst component comprising a Mg, Ti and halogen and an electron donor selected from succinates of formula (I);
- (b) an alkylaluminum compound and, optionally;
- (c) one or more electron-donor compounds (external donor).

The alkyl-Al compound (b) is preferably selected from the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use mixtures of trialkylaluminum compounds with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides, such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$.

The external donor (c) can be of the same type or it can be different from the succinate of formula (I). Suitable external electron-donor compounds include silicon compounds, ethers, esters such as ethyl 4-ethoxybenzoate, amines, heterocyclic compounds and particularly 2,2,6,6-tetramethylpiperidine, ketones and the 1,3-diethers of the general formula (II):



wherein R^{I} , R^{II} , R^{III} , R^{IV} , R^{V} and R^{VI} equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of R^{I} - R^{VI} except that they cannot be hydrogen; one or more of the R^{I} - R^{VIII} groups can be linked to form a cycle. Particularly preferred are the 1,3-diethers in which R^{VII} and R^{VIII} are selected from C_1 - C_4 alkyl radicals.

Another class of preferred external donor compounds is that of silicon compounds of formula $\text{R}_a^5\text{R}_b^6\text{Si}(\text{OR}^7)_c$, where a and b are integers from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^5 , R^6 , and R^7 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which a

is 1, b is 1, c is 2, at least one of R^5 and R^6 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R^7 is a C_1 - C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, (2-ethylpiperidiny)l-t-butyldimethoxysilane, (2-ethylpiperidiny)lthexyldimethoxysilane, (3,3,3-trifluoro-n-propyl)(2-ethylpiperidiny)l dimethoxysilane, methyl(3,3,3-trifluoro-n-propyl)dimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R^6 is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R^7 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and thexyltrimethoxysilane.

The electron donor compound (c) is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound (c) ranging from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100. As previously indicated, when used in the (co)polymerization of olefins, and in particular of propylene, the catalysts of the invention allow to obtain, with high yields, polymers having a high isotactic index (expressed by high xylene insolubility X.I.), thus showing an excellent balance of properties. This is particularly surprising in view of the fact that, as it can be seen from the comparative examples here below reported, the use as internal electron donors of unsubstituted succinate compounds gives worse results in term of yields and/or xylene insolubility.

A further advantage of the above mentioned catalyst is the capability of giving polymers having a broad molecular weight distribution even in a single polymerization step.

As mentioned above, the succinates of the present invention are also useful as external donors in catalysts for the polymerization of olefins. Accordingly, another object of the present invention is a catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (i) a solid catalyst component comprising a Mg, Ti and halogen and optionally containing an electron donor compound;
- (ii) an alkylaluminum compound and,
- (iii) one or more electron-donor compounds (external donor) selected from succinates of

formula (I).

The electron donor compound present on the catalyst component (i) can be selected from the same classes described for the electron donor (c).

According to what has been mentioned above it constitutes a particular object of the present invention a process for the (co)polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst comprising the product of the reaction between:

- (a) a solid catalyst component comprising a Mg, Ti, halogen and an electron donor selected from succinates of formula (I);
- (b) an alkylaluminum compound and, optionally,
- (c) one or more electron-donor compounds (external donor).

Said polymerization process can be carried out according to known techniques for example slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, it is possible carrying out the polymerization process in gas phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperatures ranging from 20 to 120°C, preferably from 40 to 80°C. When the polymerization is carried out in gas phase the operating pressure is generally between 0.5 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa. Hydrogen or other compounds capable to act as chain transfer agents can be used to control the molecular weight of the polymer.

The following examples are given in order to better illustrate the invention without limiting it.

CHARACTERIZATIONS

Preparation of succinates

Succinates have been prepared according to known methods described in the literature, (see for example N.R. Long, M.W. Rathke, *Synthetic Commun.* **11**, 687, 1981; M.W. Rathke, A. Lindert, *J. Am. Chem. Soc.* **93**, 460, 1971; T.J. Brocksom, N. Petragnani, R. Rodrigues, H. La Scala Teixeira, *Synthesis*, 396, 1975; J.L. Belletire, E.G. Spletzer, A.R. Pinhas, *Tetrahedron Lett.* **25**, 5969, 1984; N. Petragnani, M. Yonahiro, *Synthesis*, 710, 1980).

(TC 5405.EP)

Propylene polymerization: general procedure

In a 4 liter autoclave, purged with nitrogen flow at 70 °C for one hour, 75 ml of anhydrous hexane containing 800mg of AlEt_3 , 79.8 mg of dicyclopentyldimethoxysilane and 10 mg of solid catalyst component were introduced in propylene flow at 30 °C. The autoclave was closed. 1.5 NI of hydrogen were added and then, under stirring, 1,2 Kg of liquid propylene were fed. The temperature was raised to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. The nonreacted propylene was removed, the polymer was recovered and dried at 70 °C under vacuum for three hours and, then, weighed and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction at 25°C.

Determination of X.I.

2.5 g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer and then, by difference the xylene insoluble fraction (%).

EXAMPLES**Examples 1-16 and Comparative Examples 17-19****Preparation of solid catalyst components.**

Into a 500 ml four-necked round-bottomed flask, purged with nitrogen, 250 ml of TiCl_4 were introduced at 0°C. While stirring, 10.0 g of microspheroidal $\text{MgCl}_2 \cdot 2.8\text{C}_2\text{H}_5\text{OH}$ (prepared according to the method described in ex.2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000) and 7.4 mMoles of succinate were added. The temperature was raised to 100°C and maintained for 120 min. Then, the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

250 ml of fresh TiCl_4 were added. The mixture was reacted at 120°C for 60 min and, then, the supernatant liquid was siphoned off. The solid was washed six times with anhydrous hexane (6 x 100 ml) at 60 °C. Finally, the solid was dried under vacuum and analyzed. The type and amount of succinate (wt %) and the amount of Ti (wt %) contained in the solid

(TC 5405.EP)

catalyst component are reported in table 1. Polymerization results are reported in Table 2.

Table 1

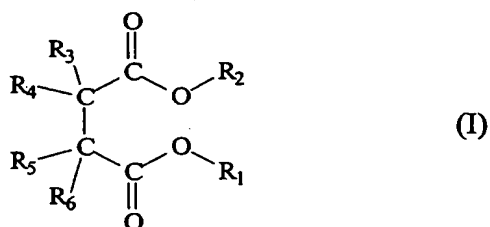
Ex.	Succinate		Ti
n.	Type	Wt %	Wt %
1	Diethyl phenylsuccinate	15.3	4.0
2	Diethyl cyclohexylsuccinate	16.4	3.3
3	Diisobutyl cyclohexylsuccinate	11.9	3.1
4	Diethyl benzylsuccinate	12.8	2.1
5	Diethyl cyclohexylmethylsuccinate	15.3	3.2
6	Diethyl 2,2-dimethylsuccinate	13.0	2.6
7	Diisobutyl 2,2-dimethylsuccinate	12.1	3.2
8	Diethyl 2-ethyl-2-methylsuccinate	13.3	1.9
9	Diisobutyl 2-ethyl-2-methylsuccinate	15.2	3.3
10	Diethyl 2,3-diisopropylsuccinate	18.9	4.2
11	Diisobutyl 2,3-diisopropylsuccinate	17.2	4.2
12	Diethyl 2,3-dibenzylsuccinate	24.1	3.2
13	Diethyl 2,3-bis(cyclohexylmethyl)succinate	21.5	4.7
14	Diisobutyl 2,2,3-trimethylsuccinate	8.0	4.4
15	Diethyl 2-benzyl-3-ethyl-3-methylsuccinate	14.9	3.2
16	Diethyl 2-cyclohexylmethyl-3-ethyl-3-methylsuccinate	17.9	2.9
Comp.17	Di-n-butyl succinate	7.4	2.1
Comp.18	Diethyl methylsuccinate	10.9	3.4
Comp.19	Diisobutyl ethylsuccinate	7.7	3.0

Table 2

Example n.	Yield KgPP/gCat.	X.I. Wt. %
1	20	98.3
2	35	97.4
3	28	97.3
4	22	96.6
5	33	97.8
6	37	97.2
7	44	97.0
8	44	98.6
9	42	97.3
10	50	98.4
11	48	98.8
12	42	96.1
13	39	97.0
14	29	96.6
15	36	96.0
16	42	96.8
Comp.17	9	96.0
Comp.18	11	95.8
Comp.19	12	96.0

CLAIMS

1. A solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising Mg, Ti, halogen and an electron donor selected from succinates of formula (I):



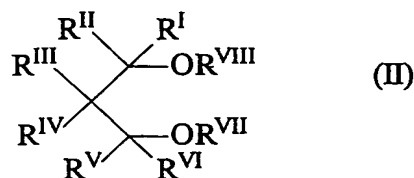
wherein the radicals R_1 and R_2 , equal to or different from each other, are a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; the radicals R_3 to R_6 equal to or different from each other, are hydrogen or a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms, further, the radicals R_3 to R_6 which are joined to the same carbon atom can be linked together to form a cycle; with the proviso that when R_3 to R_5 are contemporaneously hydrogen R_6 is a radical selected from primary branched, secondary or tertiary alkyl groups, cycloalkyl, aryl, arylalkyl or alkylaryl groups having from 3 to 20 carbon atoms.

2. Catalyst component according to claim 1 in which the electron donor compound of formula (I) is selected from those in which R_1 and R_2 are $\text{C}_1\text{-C}_8$ alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups.
3. Catalyst components according to claim 2 in R_1 and R_2 are selected from primary alkyls.
4. Catalyst components according to claim 3 in which R_1 and R_2 are selected from ethyl, isobutyl, and neopentyl.
5. Catalyst component according to claim 1 in which the electron donor compound of formula (I) is selected from those in which R_3 to R_5 are hydrogen and R_6 is a branched alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl radical having from 3 to 10 carbon atoms.
6. Catalyst component according to claim 5 in which R_6 is a branched alkyl group or a

cycloalkyl group having from 3 to 10 carbon atoms.

7. Catalyst component according to claim 1 in which the electron donor compound of formula (I) is selected from those in which at least two radicals from R_3 to R_6 are different from hydrogen and are selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups optionally containing heteroatoms.
8. Catalyst component according to claim 7 in which the two radicals different from hydrogen are linked to the same carbon atom.
9. Catalyst component according to claim 7 in which the two radicals different from hydrogen are linked to different carbon atoms.
10. A solid catalyst component according to claim 1 comprising a titanium compound having at least a Ti-halogen bond and the succinate of formula (I) supported on a Mg halide in active form.
11. A solid catalyst component according to claim 10 in which the titanium compound is $TiCl_4$ or $TiCl_3$.
12. A solid catalyst component according to claim 1 having a spherical form, a surface area (by B.E.T. method) between 20 and 500 m^2/g , preferably between 50 and 400 m^2/g , and a total porosity (by B.E.T. method) higher than 0.2 cm^3/g preferably between 0.2 and 0.6 cm^3/g .
13. A catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:
 - (a) the solid catalyst component of any of the claims 1-12;
 - (b) an alkylaluminum compound and, optionally,
 - (c) one or more electron-donor compounds (external donor).
14. Catalyst according to claim 13 in which the alkylaluminum compound (b) is a trialkyl aluminum compound.
15. Catalyst according to claim 14 in which the trialkyl aluminum compound is selected from the group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum.
16. Catalyst according to claim 13 in which the external donor (c) is selected from the 1,3-

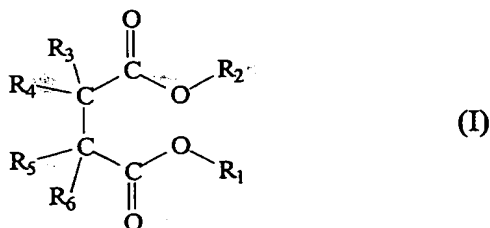
diethers of the general formula (II):



wherein R^{I} and R^{II} , R^{III} , R^{IV} , R^{V} and R^{VI} equal or different to each other, hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of $\text{R}^{\text{I}}-\text{R}^{\text{VI}}$ except that they cannot be hydrogen; one or more of the $\text{R}^{\text{I}}-\text{R}^{\text{VIII}}$ groups can be linked to form a cycle.

17. Catalyst according to claim 13 in which the external donor (c) is a silicon compound of formula $\text{R}_a^5\text{R}_b^6\text{Si}(\text{OR}^7)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 4 and the sum (a+b+c) is 4; R^5 , R^6 and R^7 are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms.
18. Catalyst according to claim 17 in which a is 1, b is 1 and c is 2.
19. Catalyst according to claim 17 in which R^5 and/or R^6 are branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R^7 is a C_1-C_{10} alkyl group, in particular methyl.
20. Catalyst according to claim 17 in which a is 0, c is 3 and R^6 is a branched alkyl or cycloalkyl group and R^7 is methyl.
21. Catalyst according to claim 17 or 19 in which the silicon compound is selected from the group consisting of methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, (2-ethylpiperidiny)t-butyldimethoxysilane, (2-ethylpiperidiny)thexyldimethoxysilane, (3,3,3-trifluoro-n-propyl)(2-ethylpiperidiny)dimethoxysilane, methyl(3,3,3-trifluoro-n-propyl)dimethoxysilane.
22. Process for the (co)polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbonyl radical with 1-12 carbon atoms, carried out in the presence of any of the catalysts of claims 13-21.

23. Substituted succinates of the following formula (I):



- wherein the radicals R_1 and R_2 , equal to or different from each other, are a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; the radicals R_3 to R_6 equal to or different from each other, are hydrogen or a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms, further, the radicals R_3 to R_6 which are joined to the same carbon atom can be linked together to form a cycle; with the proviso that when R_3 to R_5 are contemporaneously hydrogen R_6 is a radical selected from primary branched, secondary or tertiary alkyl groups, cycloalkyl, aryl, arylalkyl or alkylaryl groups, having from 3 to 20 carbon atoms.
24. Catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:
- (i) a solid catalyst component comprising a Mg, Ti and halogen and optionally containing an electron donor compound;
 - (ii) an alkylaluminum compound and,
 - (iii) one or more electron-donor compounds (external donor) selected from succinates of formula (I).
25. Use of succinates of claim 23 as electron donors in catalyst for the polymerization of olefins.

ABSTRACT

The present invention relates to a solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbon radical with 1-12 carbon atoms, comprising Mg, Ti, halogen and an electron donor selected from substituted succinates of a particular formula. Said catalyst components when used in the polymerization of olefins, and in particular of propylene, are capable to give polymers in high yields and with high isotactic index expressed in terms of high xylene insolubility.

THIS PAGE BLANK (USPTO)